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# 3D Mapping of Polymer Crosslink Density with Magnetic Resonance Imaging

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## Abstract

Magnetic Resonance Imaging (MRI) techniques have been used to detect areas of low crosslink density in damaged silicone parts in an effort to develop a QA/QC protocol to be used in the development of new parts.  Model materials of varying crosslink density first demonstrated the applicability of the method. Analysis of damaged pads has been shown to be clearly distinguishable by MRI.  It is our belief that both the $T_2$ weighted SPI NMR and the $T_2$ weighted water/fat suppression MRI experiments can be used to map out the location of different cross-linking densities, ultimately determining the quality or homogeneity in polymers.

## Introduction

Nuclear Magnetic Resonance (NMR) and Magnetic Resonance Imaging (MRI) have been extensively used for chemical, material, biological, and medical applications. NMR and MRI methods are based on the excitation and detection of the precession of nuclear moments in the presence of a large applied magnetic field by resonant radio frequency (RF) pulses.  In NMR methods, the perturbation of the applied magnetic fields induced by other sources, including nearby electrons and other nuclear moments, provides a powerful fingerprint of molecular structure.  In MRI methods, a magnetic field gradient is used in conjunction with an NMR experiment to spatially encode the spectral signatures based on numerous contrast parameters. These signatures may include structure (chemical shift), dynamics (relaxation times), or velocity (diffusion and flow) to provide spatial maps of a wealth of structural and dynamic information [1].

NMR has been used extensively to investigate structure and dynamic properties of polymers [2]. NMR parameters such as transverse ($T_2$) relaxation rates and residual dipolar coupling constants have been correlated with other chemical and mechanical tests such as DSC, GPC, and DMA to determine preliminary service lifetimes in a variety of polymers [3, 4, 5 ]. NMR offers the advantage of being able to probe simultaneously structure and dynamics *in situ*, in controlled environments, on samples of various shapes. Changes in structure can be measured directly from changes in chemical shifts. In addition, changes in crosslink density can be inferred from the resulting effects on the polymer sequential dynamics directly measurable from the NMR data.

Since NMR spectroscopy has been used to determine relative crosslink densities in polymers (i.e. the $T_2$ or spin-spin, relaxation time is proportional to $1/(CLD)^2$), MRI can offer a spatial map of the crosslink densities, which can be correlated to the overall structure homogeneity within the polymer materials [6].  Through MRI technique, a spatial three dimensional image or map of polymer properties can be obtained.

MRI techniques are being used as a QA/QC tool in the production of new outer pressure pads.  Outer pressure pad surveillance returns have exhibited local areas of permanent compression and/or rib distortion.  Numerous lab tests have been performed to try to reproduce such compression, but these tests have not succeeded in finding any conditions that lead to such damage.  It was therefore concluded that the problem lies in the production side – that is, there is a localized, uneven distribution of crosslink densities throughout the pad, leading to a lower resistance to load and a resulting damage to these parts of the pads. MRI methods are ideal to visually map out intact pressure pads.

**Experimental details**

The DC745 polymers used in this study were obtained from Dow Corning as Silastic® 745U and crosslinked with 0.55 wt% peroxide curing agent.  All MRI experiments were performed on a Bruker Avance 400MHz equipped with a high-resolution microimaging system with either a 25mm rf coil or a 5mm rf coil depending on the size of the sample.

The 2-D MRI $T_2$ weighted Single Point Imaging (SPI) for results shown in figure 1 was done with a Field-of-View (FOV) of 3.0 by 3.0cm with a resolution of 0.234mm/pixel by 0.234mm/pixel.  The excitation pulse length was 10μs, the detection time was 204.16 μs, 2 averages, and the total time was 8minutes and 13 seconds. The slice thickness is 1cm.  A similar 3D $T_2$ weighted SPI NMR experiment would take 1hour, 27minutes, and 23seconds.

The 2D $T_2$ weighted NMR experiment for the results shown in figure 3 was done with a Field-of-View (FOV) of 6.0cm by 6.0cm with a resolution of 0.234mm/pixel by 0.234mm/pixel. The slice thickness is 6cm. A similar 3D $T_2$ weighted NMR experiment would take 18hour, 12minutes, and 16seconds.  The 2D $T_2$ weighted water/fat suppression MRI experiment were taken with a echo time of 10.25ms, a repetition time of 1s, one average, and a total time of 4minutes and 16seconds.

We exposed the polymer samples to a $^{60}$Co source (1.2 MeV, 500 kRad/hour) for the appropriate time required to achieve a dose range from 0-100 MRad. Then, we preformed $T_2$ weighted water/fat suppression MRI experiments on these materials. The 2D $T_2$ weighted NMR experiment for the results shown in figure 4 was done with a Field-of-View (FOV) of 2.15cm by 2.15cm with a resolution of 0.168mm/pixel by 0.168mm/pixel. The slice thickness is 2mm. The 2D $T_2$ weighted water/fat suppression MRI experiment was taken with a echo time of 8ms, a repetition time of 1s, 4 average, and a total time of 8minutes and 34seconds.
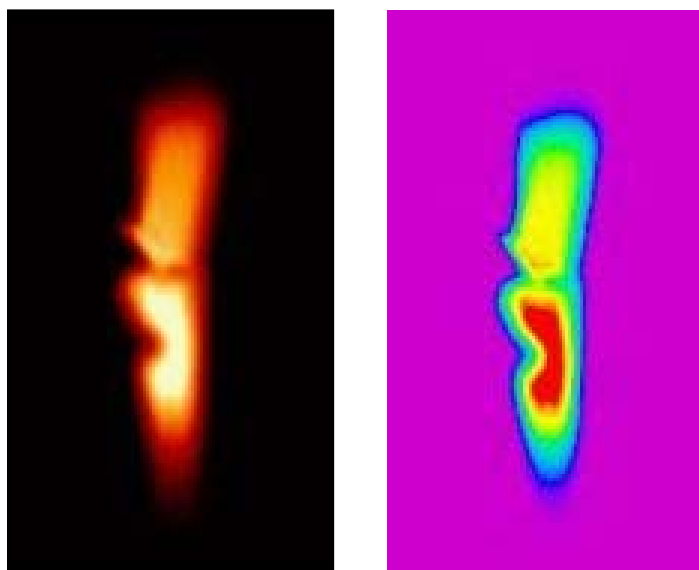


**Figure 1:** 2D $T_2$ weighted SPI on 2 DC745 samples ( Top = 0.275% catalyst and Bottom = 0.056% catalyst). The contrast parameter is $T_2$ relaxation time, with higher signal intensity ( left image = white and right image = red) indicating lower crosslink density.

## Results and discussion

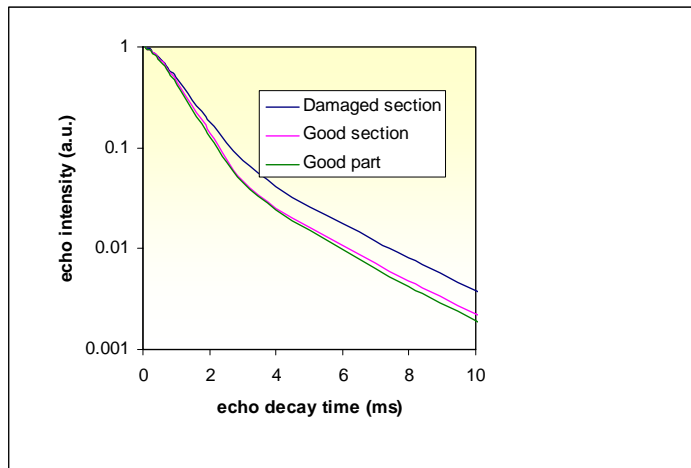To determine if MRI is an ideal method to developing a 3D map of the structure homogeneity within the polymer materials, we examined two different samples at two different cross-link densities, which have a 0.275% catalyst and 0.056% catalyst. These samples possess vastly different $T_2$ or spin-spin, relaxation time on the order of microseconds. A method known as Single Point Imaging (SPI) [7-9] was used because it enhances in the difference in very short $T_2$ relaxation times. This technique is only useful for $T_2$ relaxation times on the order of 50μs to 1ms. Since each single complex time domain data point is collected after one individual excitation and the time between the excitation and the detection stays constant for each data point, this method is not sensitive to chemical shift e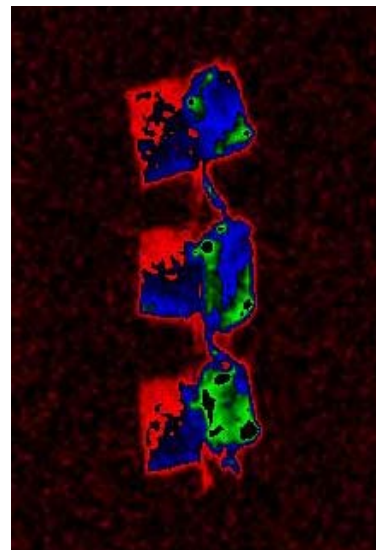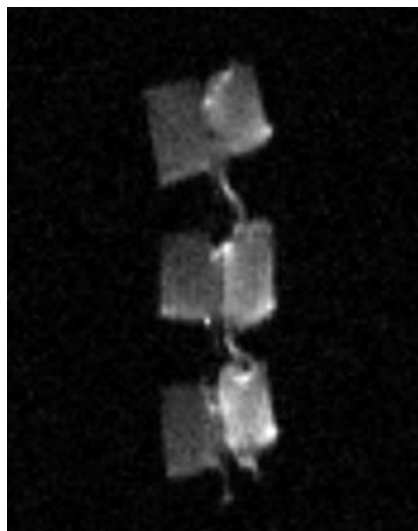volution, field inhomogeneity and local susceptibility changes in the object. However, this technique can efficiently distinguish between two very fast $T_2$ relaxation times and suppresses slow $T_2$ relaxation times. The 2-D MRI $T_2$ weighted SPI on 2 DC745 samples where the top has a 0.275% catalyst and bottom has a 0.056% catalyst.



**Figure 2:** $T_2$ curves a damaged section and pristine section of DC745.

In the case of distinguishing polymers with cross-linking densities associated with slow $T_2$ relaxation times, we used another tradition $T_2$ weighted MRI experiment that is typically used in medical MRI. $T_2$ weighted MRI is typically used in clinical applications to detect pathological tissues due to the elongated $T_2$ relaxation times; for example, high



**Figure 3:** The 2D $T_2$ weighted water/fat suppression MRI experiments of damaged section and pristine section of DC745. The contrast parameter is $T_2$ relaxation time, with higher signal intensity indicating lower crosslink density.

signals intensities occurs in tumors, which allows clinicians to distinguish between tumors and soft-tissues. A similar experiment can be used to distinguish polymers with different cross-linking densities to determine if there exists any inhomogeneities in the questionable material. A multislice multiecho experiment acquires a 2D or 3D spin echo image. This technique obtains a high contrast image on samples with $T_2$ relaxation times down to a few milliseconds. In this experiment, the magnetization of the individual slices are excited by a 90 degree pulse rf-pulses and refocused by 180 degree rf-pulses. There exists several different $T_2$ weighted MRI experiments. We choose to use a $T_2$ weighted water/fat suppression MRI experiment, which suppresses the fast $T_2$ (on the order of μs) and only gives slower $T_2$ (on the order of ms) [10]. The test sample we used contained a damaged section and pristine section of DC745. To the eye, these samples are indistinguishable. The $T_2$ curves of a damaged section and a pristine section of DC745 are shown in figure 2.

Figure 3 shows the MR Image of two different polymers where one can distinguish between the damaged section, which has a brighter signal due to the elongated $T_2$ relaxation times, and the pristine section which has a faint signal. The colored $T_2$ relaxation map in figure 3 can be used to map out the different signal intensities which is proportional to $T_2$ and can be used to map out different cross link densities.

Both the $T_2$ weighted SPI NMR and the $T_2$ weighted water/fat suppression MRI experiments can be used to map out the location of different cross-linking densities, ultimately determine the quality or homogeneity of intact polymers. Since the effects of γ-radiation and thermal degradation on siloxane polymers have been shown to lead to changes in crosslink density and motional dynamics, these changes have been measured in NMR observables such as $T_2$ relaxation times and residual dipolar couplings. We have observed trends in $T_2$ times as a function of radiation dose by high resolution NMR, namely that the $T_2$ time decreases with increasing dose. The $T_2$ weighted water/fat suppression MRI images of polymers that were exposed to different doses of radiation
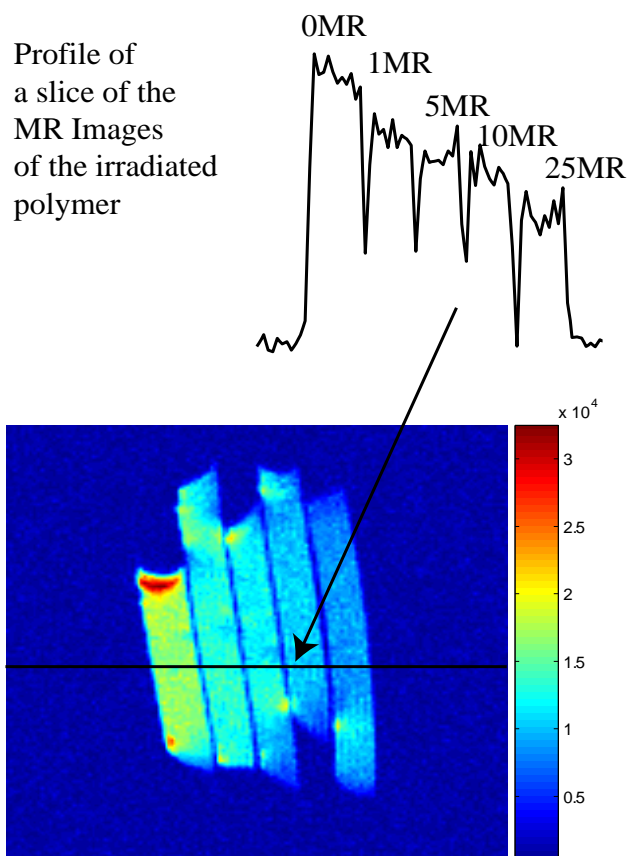


**Figure 4:** 2D $T_2$ weighted water/fat suppression MRI experiment on polymers exposed to different levels of radiation dose. The contrast parameter is $T_2$ relaxation time, with higher signal intensity indicating lower crosslink density.

are shown in Figure 4.  This figure also shows the profile of the MRI image.  In this MRI image, the contrast parameter is $T_2$ relaxation time, with higher signal intensity indicating lower crosslink density. This MRI data clearly displays the same trends as high resolution NMR, where $T_2$ decreases and cross link density increases with increasing radiation dose.

**Conclusions**

MRI is a NMR-based analytical tool used to determine relaxation times in a variety of polymeric foams and adhesives without the need to cut small pieces from intact parts.  MRI experiments can be used to map out the location of different cross-linking densities, ultimately determining the quality or homogeneity in polymers. This technique can be used as a QA/QC tool in the production process of new parts.

**Acknowledgements**

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